

# TIME-CORRELATION FUNCTIONS AND TRANSPORT COEFFICIENTS IN STATISTICAL MECHANICS<sup>1</sup>

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## INTRODUCTION

In the last decade a remarkable and fundamental development has occurred in the statistical mechanical theory of transport processes, leading to time-correlation function expressions for transport coefficients. The purposes of this review are fourfold: (a) to explain what time-correlation functions are; (b) to describe various methods that have been used to relate transport coefficients to time-correlation functions; (c) to survey some applications of time-correlation functions, particularly with reference to problems arising in physical chemistry; and (d) to indicate some potentially fruitful areas for future investigation.

The general importance of time-correlation functions is demonstrated clearly by comparison with partition functions. In equilibrium statistical mechanics, as is well known, we can find all of the thermodynamic properties of any particular system if we can first calculate its partition function. Although the actual calculation of the partition function may be exceedingly difficult (as in the case of liquids), at least we know where to start. Time-correlation functions play the same role in the theory of transport processes. For example, there is an exact formula for the coefficient of shear viscosity in terms of a certain time-correlation function. The calculation may be hard, but we know where to start.

In one respect the analogy breaks down. The state of thermal equilibrium is unique, but there are many different kinds of nonequilibrium state. A single partition function gives all thermodynamic properties, but we need a different time-correlation function for each distinct transport process. The appropriate formulas have been obtained for all transport coefficients of current interest; later in this review we give examples of some and references to where the others can be found.

## DESCRIPTION OF TIME-CORRELATION FUNCTIONS

Before embarking on a detailed review of the historical background and applications, a brief description of the essential characteristics of time-correlation functions will be instructive.

Roughly speaking, we obtain a time-correlation function when we take some time dependent quantity  $A(t)$ , multiply it by another time dependent quantity  $B(t')$  evaluated at some different time  $t'$ , and then average the product over some equilibrium ensemble. A more precise definition follows.

Time-correlation functions occur in both classical and quantum statistical

<sup>1</sup> The survey of literature pertaining to this review was concluded in November 1964.

mechanics. The quantum mechanical theory is naturally more general and must include the corresponding classical formulas as limiting cases. Since the classical theory is somewhat easier to describe, we shall do this first, and then show what modifications have to be made in the quantum theory. (In the following part of this review, devoted to several methods used to relate transport coefficients to time-correlation functions, we begin with one derivation using quantum mechanics, and thereafter restrict the discussion to classical mechanics.)

In classical mechanics, the dynamical state of any system is specified by giving the coordinates  $q_1, q_2, q_3, \dots$  and the conjugate momenta  $p_1, p_2, p_3, \dots$  of all degrees of freedom at any particular time  $t$ . For convenience we often use the single symbol  $q$  or  $p$  to denote the set of all coordinates and momenta, and  $\int dq$  or  $\int dp$  to denote integration over all of coordinate or momentum space.

The time dependence of the coordinates  $q(t)$  and momenta  $p(t)$  is obtained by solving the equations of motion of the entire system. When Hamilton's equations of motion are used, there is one first-order differential equation for each coordinate or momentum; thus the solution contains one arbitrary constant for each coordinate or momentum. These constants are conveniently picked as the values  $q(0)$  and  $p(0)$  at the initial time  $t=0$ . (In the following, we often leave out the  $(0)$ , with the understanding that when no specific time is mentioned, the initial time is meant.) Then the solution of the equations of motion takes the form of a function of  $t$ ,  $q$ , and  $p$ ; for example,  $q(t; q, p)$  is the coordinate at time  $t$ , expressed as a function of the coordinates  $q$  and momenta  $p$  at the initial time  $t=0$ .

Now let us consider some function  $A(p, q)$  of the state of the system. This function does not necessarily have to depend on all the variables. In one useful example, associated with the self-diffusion coefficient, the function  $A$  is just the momentum of the "tagged" molecule under observation. The numerical value of  $A$  at time  $t$  depends on the coordinates and momenta at  $t$ , and thus it depends on the time and on the initial values  $p$  and  $q$ , or

$$A(p(t), q(t)) = A(t; p, q) = A(t)$$

We frequently leave implicit the dependence on initial values and write just  $A(t)$ .

The time-correlation function of  $A$  is then defined as the ensemble average  $\langle \cdot \rangle$  of the product of the initial  $A$  and the value of  $A$  at time  $t$ ,  $\langle A(0)A(t) \rangle$ . On introducing the equilibrium phase space distribution function  $f(p, q)$ , the ensemble average is given more explicitly by

$$\langle A(0)A(t) \rangle = \int dp \int dq A(p, q) A(t; p, q) f(p, q)$$

In just the same way we may define time-correlation functions of different variables, viz.  $\langle A(0) B(t) \rangle$

Because the choice of origin of the time scale is entirely arbitrary, and be-

cause the equilibrium ensemble distribution function is invariant to displacement of time, we have the obvious identity

$$\langle A(t)B(t') \rangle = \langle A(0)B(t' - t) \rangle$$

The formulas for transport coefficients to be discussed in this review all have the general structure of a one-sided Fourier transform (or a complex Laplace transform) of a time-correlation function,

$$\sigma(\omega) = \int_0^{\infty} dt \exp(-i\omega t) \langle \dot{A}(0) \dot{B}(t) \rangle$$

It should be observed that the variables in the time-correlation function are time derivatives, e.g.,  $\dot{A} = dA/dt$ , and not the functions themselves. The variable  $\omega$  in the transform may be regarded as a frequency. We suppose that it has a small negative imaginary part, if necessary, to provide convergence. (Usually one calculates transport coefficients in the limit of an infinitely large system—the “thermodynamic limit”; if this limit is taken first, there are no special convergence difficulties, and the small negative imaginary part is not needed.) In most applications, only the low frequency behavior

$$\lim_{\omega \rightarrow 0-i\epsilon} \sigma(\omega)$$

is of interest. (We have indicated the small negative imaginary part explicitly in this limit.)

It may seem at first that in order to calculate a transport coefficient by means of time-correlation functions, one has to perform the almost impossible task of solving the general  $N$ -body problem. As we shall see, the situation is actually not so bad. For example, we need only the time dependence of certain special quantities  $\dot{A}$  ( $p, q$ ) and this information may be considerably easier to get than the complete solution of the equations of motion. (As a trivial but illustrative example, consider the function  $A$  = total energy. This is in fact a constant of the motion, so we know its time dependence without solving equations of motion at all.)

Furthermore, we need only the time dependence of an ensemble average. It turns out in many cases that the ensemble average eliminates a substantial amount of the complexity of the exact solution of the equations of motion. This is particularly clear in certain calculations on crystal lattices in the harmonic approximation (1).

A final simplification arises from the special emphasis put on low frequency components of time-correlation functions, which involve only rather gross features of the exact time dependence. For example, in calculating the viscosity of a gas at low density, we find that we do not need molecular collision trajectories in complete detail; only the asymptotes of these trajectories are relevant. The reason is that a collision has a very short duration, perhaps  $10^{-12}$  sec, so that the complete history of a collision is associated with frequencies of the order of  $10^{12}$  sec $^{-1}$ .

The nature of the functions  $A(p, q)$ , the ensemble average, and the low

frequency limit all serve to make calculations more practical. Later in this review we discuss some examples where calculations have been performed successfully.

The quantum mechanical expressions for transport coefficients are somewhat more complicated, although in a way that is not really relevant to most of the applications that we discuss here. We use units where  $\hbar = 2\pi$ .

Five changes have to be made. (a) The functions  $A$  are replaced by their corresponding quantum mechanical operators. (b) The equilibrium phase space distribution function is replaced by the equilibrium density matrix  $\rho$ . (c) The ensemble average is calculated by taking the trace of the operator product,

$$\langle A \rangle = \text{Trace} (\rho A)$$

(d) The time derivative of the operator  $A$  is given by Heisenberg's equation of motion,

$$dA/dt = i[H, A]$$

where  $H$  is the Hamiltonian operator of the entire system. The solution of this equation of motion is written as the time dependent operator

$$A(t) = e^{itH} A e^{-itH}$$

(e) Finally, the definition of the time-correlation function is modified by introduction of the "Kubo transform." [This terminology is due to Jaynes (2).] The Kubo transform of an operator  $A$  is another operator  $\tilde{A}$  defined by

$$\tilde{A} = \frac{1}{\beta} \int_0^\beta d\lambda (\exp \lambda H) A (\exp -\lambda H)$$

We use the standard abbreviation  $\beta = 1/k_B T$ , where  $k_B$  is Boltzmann's constant and  $T$  is absolute temperature.

With the preceding five changes, transport coefficients in quantum mechanics have the form

$$\sigma(\omega) = \int_0^\infty dt \exp(-i\omega t) \langle \tilde{A}(0) \dot{B}(t) \rangle$$

From the standpoint of notation, the only evident difference between the classical and the quantum mechanical expressions lies in the presence of the Kubo transform; and at sufficiently high temperatures (as required for a classical limit) the Kubo transform of an operator is just the operator itself.

#### DERIVATION OF FORMULAS

This part of the review deals principally with the various methods that have been used to establish connections between time-correlation functions and transport coefficients. Discussion of the resulting formulas and their use in physical chemistry is reserved for the following part.

Most of the discussion is about work published since 1950. Earlier work on correlation functions and transport coefficients was concerned primarily with the theory of Brownian motion and its relation to electrical noise (Ny-

quist noise). A chapter in the textbook *Statistical Mechanics* by Davidson (3) gives an elementary introduction to this material. A more thorough treatment may be found in *Elementary Statistical Physics* by Kittel (4); this book contains most of the important references to the earlier work. *Statistical Physics* by Landau & Lifshitz (5) is another valuable source.

Theoretical connections between time-correlation functions and transport coefficients have been investigated from many points of view. A convenient and very natural classification of methods distinguishes between transport processes driven by external forces and transport processes associated with internal (or thermodynamic) forces.

In the first category, the response of an equilibrium system to an externally imposed force, the theory is simple and straightforward. The standard reference here is a 1957 article by Kubo (6); a somewhat more pedagogic version is contained in Kubo's Boulder Lectures (7).

It should be noted, however, that the basic idea was in the air for some time before 1957. We mention in particular the work of Callen & Welton (8) and Callen & Greene (9) on the fluctuation-dissipation theorem. A review by Bernard & Callen (10) provides an excellent and comprehensive survey of this work. The textbooks of Landau & Lifshitz (5) and Kittel (4) discuss Callen's work.

Kubo's method for handling the external force problem has become so popular in the last few years that the results obtained not only by this method, but also by entirely unrelated methods, are often called "Kubo formulas." This terminology is unfortunate and should be avoided. The results referred to in this way were, for the most part, obtained by others and at earlier times. We mention in particular the work of Green (11, 12), to be described shortly.

Kubo's *method* is especially attractive because of its simplicity and its strongly operational character. Consider, for example, the application of this method to the theory of electrical conductivity.

In its most elementary form, a measurement of electrical conductivity consists of observing the electric current in response to an applied electric field. Because a single measurement is usually not enough to establish a law of nature—some accident, or even an extraordinarily large thermal fluctuation, may have occurred—the measurement is repeated many times, and the results are averaged. Then the conductivity is defined by the relation of average electric current ( $J$ ) to applied field  $E$ ,

$$\langle J \rangle = \sigma E + O(E^2)$$

(The electric field is taken small enough that nonlinear effects are of no importance.)

More often, the frequency dependence of the electrical conductivity is of interest. To measure this quantity, one switches on an arbitrary time-dependent electric field  $E(t)$  at  $t=0$ , and one then measures the average current  $\langle J(t) \rangle$ . The observed relation between  $\langle J(t) \rangle$  and  $E(t)$  is

$$\langle J(t) \rangle = \int_0^t dt' \Phi(t-t') E(t') + O(E^2)$$

where  $\Phi(t-t')$  is an “after-effect function” showing the response at  $t$  to a disturbance at  $t'$ . Frequency components of the current and field are defined by Fourier analysis,

$$\langle J_\omega \rangle = \int_0^\infty dt \exp(-i\omega t) \langle J(t) \rangle$$

$$E_\omega = \int_0^\infty dt \exp(-i\omega t) E(t)$$

Note that the lower limit on these integrals is  $t=0$  and not the more conventional  $t=-\infty$ ; this is because the field and current are both zero before the field is switched on. By an easy rearrangement of the integrals, we obtain

$$\langle J_\omega \rangle = \delta(\omega) E_\omega$$

where  $\delta(\omega)$  is the frequency dependent conductivity,

$$\delta(\omega) = \int_0^\infty dt \exp(-i\omega t) \Phi(t)$$

Kubo's statistical mechanical theory is just a general model of the above experiments. The method, while simple and direct, relies on certain abstract operator techniques that may not be familiar to most physical chemists. To show just how simple it is, we present here a version of the derivation that relies only on methods to be found in most elementary quantum mechanics textbooks. (The derivation, in this case, is no more difficult in quantum mechanics than it is in classical mechanics, so the quantum mechanical version is given for the sake of generality.)

We note first that there are three stages to an experiment on electrical conductivity: the initial preparation of the system, the switching on of the field, and the measurement of the current. Each of these stages has its analogue in the statistical mechanical theory.

In the first stage, the experimenter prepares the system in a “state of thermal equilibrium.” It is important to know just what this means. The experimenter does not actually control the exact state of the system, in the sense of specifying in all detail the wave function of the system, or its position in phase space. All he can do is select a sample, for example a piece of wire, according to some prescription. To repeat the experiment he selects another sample, according to the same prescription, and so on. The most likely prescription for an experiment of this sort is that the samples are to be taken at random from a spool of wire, or perhaps from many spools of wire that are themselves chosen at random. That is, the experimenter takes samples from an ensemble. To say that the system is prepared in a state of thermal equilibrium is to say that repetitions of an experiment are performed on samples taken from a thermal equilibrium (canonical) ensemble.

Let  $H_0$  be the total Hamiltonian operator of the system (in the absence of any applied field). The exact eigenfunctions  $\psi_n$  and eigenvalues  $E_n$  of  $H_0$  are determined by

$$H_0\psi_n = E_n\psi_n$$

In the representation determined by these exact (unperturbed) eigenstates, the equilibrium density matrix is diagonal,

$$(\rho)_{mn} = \rho_n \delta_{mn}$$

and  $\rho_n$  is the probability of observing the system in the state  $\psi_n$ ,

$$\rho_n = Q^{-1} \exp - \beta E_n$$

We use the standard abbreviation  $\beta = 1/k_B T$ . The partition function  $Q$  is

$$Q = \sum_n \exp - \beta E_n$$

Thus the average behavior observed in repeated experiments is found by calculating the actual behavior of a particular eigenstate  $\psi_n$ , followed by averaging over the canonical distribution of eigenstates.

In the second stage of an experiment, an external field  $E(t)$  is switched on. For convenience we suppose that the field is directed along a cartesian coordinate axis, labeled by  $a = 1, 2$ , or  $3$ . The field interacts with the total electric dipole moment  $M$  of the system,

$$M = \sum_j e_j R_j$$

where  $e_j$  and  $R_j$  are the charge and position of the  $j$ -th particle. We assume that the field is spatially uniform over the system. Then the energy of interaction is described by the perturbation Hamiltonian

$$H_1(t) = - M_a E_a(t)$$

Because the field points in the  $a$ -th direction, only the  $a$ -th component of the moment appears in  $H_1$ .

The state  $\psi(t)$  of the system at time  $t$  is determined by solving the time-dependent Schrodinger equation

$$i \frac{\partial \psi}{\partial t} = (H_0 + H_1(t))\psi(t)$$

subject to the initial condition that  $\psi(0)$  equals  $\psi_n$  with probability  $\rho_n$ .

It is now an elementary calculation in time-dependent perturbation theory to find  $\psi(t)$ . To the first order in the applied field, the result is

$$\psi(t) = \psi_n e^{-iE_n t} + \sum_{m \neq n} \frac{1}{i} \int_0^t dt' e^{i(E_m - E_n)t'} [H_1(t')]_{mn} \psi_m e^{-iE_m t} + O(H_1^2)$$

In the third stage of the experiment, the current is measured. This corresponds, in the statistical mechanical theory, to calculating the expecta-

tion value of the current operator  $J$ , first with respect to the state  $\psi(t)$  and then with respect to the canonical distribution of initial states.

The component  $J_b$  of electric current in the  $b$ -th direction is

$$J_b = \sum e_i(\dot{R}_i)_b = \dot{M}_b$$

Its average value at time  $t$ , for the given initial state  $\psi_n$ , is

$$\begin{aligned} \int dR\psi^*(t) J_b \psi(t) &= (J_b)_{nn} + \sum_{m \neq n} \frac{1}{i} \int_0^t dt' (J_b)_{nm} e^{-i(E_m - E_n)(t-t')} [H_1(t')]_{mn} \\ &\quad - \sum_{m \neq n} \frac{1}{i} \int_0^t dt' (J_b)_{mn} e^{-i(E_n - E_m)(t-t')} [H_1(t')]_{nm} + O(H^2) \end{aligned}$$

Next, we average this result over the canonical distribution of initial states; we put in the explicit formula for  $H_1$  in terms of the electric moment and the electric field; and we rearrange the terms slightly. The result can be put in the form

$$\langle J_b(t) \rangle = \langle J_b \rangle_{eq} + \int_0^t dt' \phi_{ba}(t-t') E_a(t') + O(E^2)$$

where  $\langle J_b \rangle_{eq}$  is the average current at equilibrium, and vanishes,

$$\langle J_b \rangle_{eq} = \sum_n \rho_n (J_b)_{nn} = 0$$

and  $\phi_{ba}$  is the after-effect function giving the current in the  $b$ -th direction due to a field in the  $a$ -th direction,

$$\phi_{ba}(t) = \sum_{m \neq n} \sum_n \rho_n(i)^{-1} \{ e^{i(E_m - E_n)t} (J_b)_{mn} (M_a)_{nm} - e^{i(E_n - E_m)t} (J_b)_{nm} (M_a)_{mn} \}$$

Matrix elements of the electric moment can be expressed in terms of matrix elements of the current by means of the Heisenberg equation of motion

$$\langle J \rangle_{mn} = \langle \dot{M} \rangle_{mn} = - \langle i \rangle^{-1} (E_m - E_n) \langle M \rangle_{mn}$$

The time-dependent current operator  $J(t)$  has matrix elements

$$\langle J(t) \rangle_{mn} = e^{i(E_m - E_n)t} \langle J \rangle_{mn}$$

With use of the preceding two equations, and by some further algebraic rearrangement, we obtain the following expression for  $\phi_{ba}$ :

$$\phi_{ba}(t) \approx \sum_m \sum_n \rho_m (J_a)_{mn} [J_b(t)]_{nm} \frac{e^{-i(E_n - E_m)t} - 1}{E_m - E_n}$$

Now we refer back to the formula given earlier for the Kubo transform, viz.

$$\tilde{J}_a = \frac{1}{\beta} \int_0^\beta d\lambda e^{\lambda H} J_a e^{-\lambda H}$$

The matrix elements of  $\tilde{J}_a$  are

$$\begin{aligned} \langle \tilde{J}_a \rangle_{mn} &= \frac{1}{\beta} \int_0^\beta d\lambda e^{\lambda(E_m - E_n)} (J_a)_{mn} \\ &= \frac{1}{\beta} \frac{e^{-\beta(E_n - E_m)} - 1}{E_m - E_n} (J_a)_{mn} \end{aligned}$$

Consequently we may write  $\phi$  in the form

$$\phi_{ba}(t) = \beta \sum_m \sum_n p_m \langle \tilde{J}_a \rangle_{mn} [J_b(t)]_{nm}$$

But by the rule of matrix multiplication and the definition of the canonical average, this is just

$$\phi_{ba}(t) = \beta \langle \tilde{J}_a J_b(t) \rangle$$

Thus  $\phi(t)$  is a time-correlation function. The corresponding frequency dependent electric conductivity tensor is

$$\sigma_{ba}(\omega) = \beta \int_0^\infty dt \exp(-i\omega t) \langle \tilde{J}_a J_b(t) \rangle$$

Several comments about this remarkably simple theory are in order.

(a) Kubo's original derivation was considerably more concise than the one given here, largely as a result of his systematic use of abstract operator techniques.

(b) The corresponding formulas in classical statistical mechanics are obtained, as already pointed out, by omitting the Kubo transform, calculating the time dependence by means of classical mechanics, and performing the ensemble average by integration over phase space. In Kubo's article (6), the classical formula is also obtained by direct calculation using classical statistical mechanics, rather than by appeal to a correspondence argument.

(c) Often in discussions of the theory of irreversible processes, the question arises "Where was the irreversibility put into the theory?" In the present case the answer is simple. Irreversible behavior is surely observed in the real world. If statistical mechanics, as applied here, is a good model of phenomena in the real world, then irreversible behavior must be accounted for automatically, without any conscious effort to "put it in." (In this connection it should be noted that some of the famous irreversibility "paradoxes" are avoided in a very simple way by calculating time-correlation functions in the limit of an infinitely large system. This limit is mainly a mathematical convenience, serving to eliminate recurrences occurring at such distant times that they would never be observed anyway.)

(d) While the transport process under consideration was electric conductivity, the method obviously can be used for any process driven by an external field: for example, sedimentation in a centrifugal field. Kubo approached the general theory by way of its application to the theory of line width in nuclear magnetic resonance spectra (13).

(e) If we had calculated the response in the form of induced polarization rather than induced current, we would have obtained an expression for the

dielectric response (macroscopic polarizability) instead of the conductivity. Inspection of the derivation will show that the principal difference in the results lies in the role of real and imaginary parts. That is, the imaginary part of the conductivity describes a dielectric response; and the imaginary part of the dielectric constant describes a conductive response. Thus, both kinds of response are accounted for at the same time. This topic, together with the further complications due to magnetic effects, has been discussed by Blatt & Matsubara (14). We return to the relation of time-correlation functions and dielectric theory in the following part of this review.

In connection with the last two remarks, we give here for the sake of completeness the most general result obtained by Kubo's method.

Let us consider situations where the perturbing Hamiltonian consists of a number of terms, each of which has the form of some property of the system  $A_j$ , multiplied by some kind of field  $E_j(t)$ ,

$$H_1 = - \sum_j A_j E_j(t)$$

(Because of the linearity of first order perturbation theory, the effects of the various fields are additive, so they can be treated independently.) The response of the system to the fields will be expressed in terms of certain arbitrary currents  $B_j = J_j$ ,

$$\langle J_j(t) \rangle = \sum_i \int_0^t dt' \phi_{ji}(t-t') E_i(t') + O(E^3)$$

or, in Fourier components (in analogy with the electrical conductivity theory)

$$\langle J_j(\omega) \rangle = \sum_i \sigma_{ji}(\omega) E_i(\omega)$$

The transport coefficients  $\sigma_{ji}(\omega)$  are given by

$$\sigma_{ji}(\omega) = \beta \int_0^\infty dt \exp(-i\omega t) \langle \tilde{A}_i(0) B_j(t) \rangle$$

which is the general form that we referred to in the first part of this review.

*Thermal processes.*—Transport coefficients associated with internal disturbances (or thermal forces) cannot be treated directly by Kubo's method. For example, there does not appear to be any convincing way of representing the effects of a temperature gradient by means of a perturbation Hamiltonian. However, many other methods have been investigated. We propose to describe here the essential features of some of them.

Among the variety of methods that have been devised for treating thermal processes, we may distinguish between six general approaches, grouped for convenience under the headings:

(a) indirect Kubo, (b) Fokker-Planck, (c) regression hypothesis, (d) local equilibrium, (e) external reservoir, and (f) prediction theory.

Before discussing these approaches, we observe that while rather different in character, they all lead to identical values for transport coefficients. For this reason, any expressed preference for one approach over the others must be regarded as a matter of individual taste in such questions as rigor, elegance, and simplicity.

[Certain apparent discrepancies between results obtained, by means of different methods, by Green (12), Mori (15, 16), and McLennan (17), have been resolved by Green (18) and McLennan (19). The point here was that time-correlation functions, being second moments of fluctuating quantities, must depend on the ensemble used. Thus, the time-correlation function of a particular quantity  $A$ , calculated in one ensemble, may correspond to the time-correlation function of a somewhat different quantity  $A'$  in another ensemble. On allowing for the effects of changing ensembles, the resulting formulas for transport coefficients give identical numerical values. Having once noted this potential source of confusion, we shall not refer to it again.]

The consensus of workers in this field seems to be that the indirect Kubo method is the most convincing approach presently available. Also, it is by far the easiest to explain, since it relies mainly on a clever application of Kubo's method for external forces. The principal references to the indirect Kubo method are by Luttinger (20), Kadanoff & Martin (21), Jackson & Mazur (22), Felderhof & Oppenheim (23), and Montroll (24).

The gist of the indirect Kubo method is best explained by an illustration drawn from hydrodynamics. At time  $t=0$ , an external body force  $\mathbf{F}(\mathbf{R}, t)$  is applied to a fluid originally in thermal equilibrium. This force causes fluid motion, and in particular, it gives rise to a certain velocity field  $\mathbf{v}(\mathbf{R}, t)$ . The relation between the force and the response is most conveniently expressed in terms of Fourier components, viz.

$$\begin{aligned}\mathbf{F}(\omega, \mathbf{k}) &= \int d^3R \int dt \mathbf{F}(\mathbf{R}, t) \exp(-i\mathbf{k} \cdot \mathbf{R} + i\omega t) \\ \mathbf{v}(\omega, \mathbf{k}) &= \int d^3R \int dt \mathbf{v}(\mathbf{R}, t) \exp(-i\mathbf{k} \cdot \mathbf{R} + i\omega t)\end{aligned}$$

On solving the hydrodynamic equations of motion (for sufficiently small forces that these equations may be linearized in deviations from equilibrium), one obtains a simple relation between  $\mathbf{v}$  and  $\mathbf{F}$ ,

$$\mathbf{v}(\omega, \mathbf{k}) = \sigma(\omega, \mathbf{k}) \mathbf{F}(\omega, \mathbf{k})$$

When the force is transverse, i.e., when  $\nabla \cdot \mathbf{F} = 0$  and  $\nabla \times \mathbf{F} \neq 0$ , then the velocity field is also transverse. In this case, the coefficient  $\sigma(\omega, \mathbf{k})$  is

$$\sigma(\omega, \mathbf{k}) = [\eta k^2 - i\omega\rho]^{-1}$$

The mass density of the fluid is  $\rho$ , and  $\eta$  is the coefficient of shear viscosity. We emphasize that the calculation leading to this equation is entirely macroscopic in character, being based solely on the known validity of the Navier-Stokes equation.

The coefficient of shear viscosity can be extracted from  $\sigma$  by first going to the limit of long wavelength (or small  $k$ ), and then going to the limit of low frequency, as follows:

$$\eta = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{\rho^2 \omega^2}{k^2} \operatorname{Re} \sigma(\omega, k)$$

This can be seen, for example, by expanding  $\sigma$  in powers of  $k$ .

But  $\sigma(\omega, k)$  can be obtained by Kubo's method! The force  $\mathbf{F}(R, t)$  is in fact externally imposed, and  $v(R, t)$  is a dynamical response of the system to that force. Application of Kubo's method leads to a statistical mechanical formula for  $\sigma(\omega, k)$ . When the indicated limits are taken, a statistical mechanical formula for the coefficient of shear viscosity is obtained. The result, first obtained by Green (12) by an entirely different method, will be given in the part of this review devoted to applications.

An essential feature of the argument just outlined is that the force was taken to be transverse, with zero divergence and nonzero curl. This is somewhat unusual; most forces that one is accustomed to deal with are conservative, so that they are expressed as the gradient of a potential. But then they automatically have zero curl, and cannot be transverse. We may, however, imagine a fictitious transverse force of the following kind. Suppose that each molecule of the fluid is given an infinitesimal electric charge. Then the force exerted on these charges by the electric field of a plane polarized light wave is transverse.

The fact that this experiment can be performed only in thought and not in the laboratory is irrelevant. There is no reason to believe that the Navier-Stokes equation fails for fictitious transverse forces, any more than that Newton's equations of motion fail for such forces.

A similar thought experiment is required for thermal conductivity. In Luttinger's treatment (20), the force comes from the interaction of a varying gravitational field with the mass associated with the internal energy of a fluid ( $E = mc^2!$ ).

While the indirect Kubo method is perhaps the most convincing one developed up to now, it serves only to re-derive results already obtained by other methods. The first theory to yield useful results is the one we categorize as the Fokker-Planck theory.

This approach is based on ideas that are familiar in the theory of Brownian motion. The movement of a Brownian particle in a fluid is governed by three different kinds of force: (a) a force due to external sources, for example, the force exerted on a charged particle by an electric field; (b) a force due to friction, generally given by Stokes' law; and (c) a force due to random weak interactions of the Brownian particle with the molecules of the surrounding fluid. Because of the random nature of part of the total force, the motion of the Brownian particle is irregular. This suggests the use of probability methods in describing Brownian motion.

Let  $P(R_0, t_0/R, t)$  be the probability (per unit volume) of finding the

Brownian particle at position  $\mathbf{R}$  at time  $t$ , given its position  $\mathbf{R}_0$  at time  $t_0$ . This function is determined by the fundamental equation of the theory of Brownian motion, the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \nabla \cdot (\mathbf{A}P) + \nabla^2(DP)$$

Many texts give derivations of this equation: see Kittel (4).

The coefficients  $\mathbf{A}$  and  $D$  appearing in the Fokker-Planck equation have a simple meaning. Denote by  $\Delta \mathbf{R}$  the displacement of the Brownian particle during a time interval  $\Delta t$ . Then in the course of the derivation of the Fokker-Planck equation, one finds that  $\mathbf{A}$  is expressed in terms of the ensemble average  $\langle \Delta \mathbf{R} \rangle$  as follows:

$$\mathbf{A} = \lim_{\Delta t \rightarrow 0} \langle \Delta \mathbf{R} \rangle / \Delta t$$

That is,  $\mathbf{A}$  is an average velocity. It must be noted that the limit  $\Delta t \rightarrow 0$  has a special meaning in this context. The time interval  $\Delta t$  is to be small in a macroscopic sense, but still larger than all characteristic molecular times. That is, many individual interactions between the Brownian particle and the surrounding molecules will occur during  $\Delta t$ , but the particle will not move appreciably during  $\Delta t$ .

The coefficient  $D$  is determined by the second moment of the displacement,  $\langle (\Delta \mathbf{R})^2 \rangle$ , according to

$$D = \lim_{\Delta t \rightarrow 0} \langle (\Delta \mathbf{R})^2 \rangle / 6\Delta t$$

Higher moments of the displacement are treated as negligible in the customary derivation of the Fokker-Planck equation.

The formula just given for  $D$  is in fact a way of writing an important equation due to Einstein,  $\langle R^2 \rangle_{av} = 6Dt$ . Evidently  $D$  is just the coefficient of self-diffusion. This provides in principle a molecular theory of the diffusion coefficient which involves a time-correlation function. To see how this goes, let us replace the displacement by a time integral of the velocity of the Brownian particle,

$$\Delta \mathbf{R} = \int_0^{\Delta t} ds \mathbf{v}(s)$$

Then the definition of  $D$  leads to

$$D = \lim_{\Delta t \rightarrow 0} (6\Delta t)^{-1} \int_0^{\Delta t} ds \int_0^{\Delta t} ds' \langle \mathbf{v}(s) \cdot \mathbf{v}(s') \rangle$$

Note that the integrand contains the time-correlation function of the velocity of the Brownian particle. Because of invariance to any change in the origin of the time axis

$$\langle \mathbf{v}(s) \cdot \mathbf{v}(s') \rangle = \langle \mathbf{v}(0) \cdot \mathbf{v}(s' - s) \rangle$$

one of the time integrals can be performed immediately, leading to

$$D = \lim_{\Delta t \rightarrow 0} \frac{1}{3} \int_0^{\Delta t} ds (1 - s/\Delta t) \langle \mathbf{v}(0) \cdot \mathbf{v}(s) \rangle$$

Suppose now that the time-correlation function tends to zero over times of a molecular order of magnitude. Then, for time intervals  $\Delta t$  that are small but yet macroscopic, the term  $s/\Delta t$  may be omitted—

$$D \cong \frac{1}{3} \int_0^{\Delta t} ds \langle \mathbf{v}(0) \cdot \mathbf{v}(s) \rangle$$

Parenthetically, we mention that the rigorous theory of self-diffusion leads to a very slightly different result,

$$D = \lim_{\epsilon \rightarrow 0} \frac{1}{3} \int_0^{\infty} dt \exp(-\epsilon s) \langle \mathbf{v}(0) \cdot \mathbf{v}(s) \rangle$$

The previous condition on the size of  $\Delta t$  is replaced by an extra limiting process.

In 1946, Kirkwood (25) presented a molecular theory of Brownian motion that was meant to apply to the motion of an individual molecule in a medium composed of similar molecules (e.g., self-diffusion in liquid argon). In comparison with the elementary theory just described, one essential difference is that Kirkwood's theory was concerned with Brownian motion in momentum space. He derived a Fokker-Planck equation in momentum space; and in the course of the derivation, he found a molecular formula for the friction constant.

Let  $\langle \mathbf{p} \rangle$  be the average momentum of a molecule in a liquid, and let  $M$  be its mass. Then the friction constant is defined as the coefficient in the frictional retarding force on the molecule,

$$\frac{d\langle \mathbf{p} \rangle}{dt} = -\xi \langle \mathbf{p} \rangle / M$$

Kirkwood's expression for  $\xi$  takes the form of a time-correlation function formula in the instantaneous force  $\mathbf{F}(t)$  exerted on the molecule by its surroundings,

$$\xi = \frac{1}{3} \beta \int_0^{\tau} dt \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle$$

The upper limit  $\tau$  is supposed to be macroscopically short, but long compared with characteristic molecular times. For a review of Kirkwood's theory, see Rice & Frisch (26).

It is important to observe that the preceding result gives a "transport coefficient" associated with momentum, and that it involves a time-correlation function in the time derivative of the momentum. This is analogous to the formula for the diffusion coefficient  $D$  of a Brownian particle, associated with the position of the particle, which involves a time-correlation function in the time derivative of the position.

Kirkwood's theory is not exact, and there is still considerable question as

to the limits of its validity. By a different method, however, Lebowitz & Rubin (27) have shown the correctness of Kirkwood's results in a limiting case, where the mass  $M$  of the Brownian particle is very much larger than the mass of any of the surrounding molecules. (This restriction actually excludes Kirkwood's application to monatomic fluids.) The exact formula for  $\zeta$  in the heavy mass limit is

$$\zeta = \lim_{\epsilon \rightarrow 0} \frac{1}{3} \beta \int_0^{\infty} dt \exp(-\epsilon t) \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle$$

Because of the heavy mass limit, the motion is to be calculated with the Brownian particle held fixed in space.

In 1952 and 1954, Green (11, 12) presented an important generalization of Kirkwood's work. The new feature supplied by Green's theory was the introduction of Brownian motion ideas into the general theory of irreversible processes.

In experiments on transport processes, certain specific properties of a system are observed as functions of time. These properties may be, for example, the local mass density of a fluid, its velocity field, its local energy density, etc. Green refers to them as "gross variables." We shall denote these quantities by  $A_1, A_2, A_3, \dots$ ; and collectively, by  $A$ .

The gross variables, being dynamical quantities, are functions of time. On the average, their time dependence is described by well-known transport laws, e.g., Fick's law of diffusion. In any individual experiment, however, apparently random small fluctuations from the average behavior will be seen, as a result of the molecular many-body character of a macroscopic system. This situation is reminiscent of the one in Brownian motion, where the path of the Brownian particle is regular on the average, but subject to small random fluctuations.

Green introduced a probability distribution function  $g(a; t)$  in the space of the gross variables: the probability of the event  $a < A < a + da$  at time  $t$  is  $g(a; t)da$ . He then gave persuasive arguments that  $g(a; t)$  should satisfy an equation having the Fokker-Planck structure. By arguments very much like those used by Kirkwood to derive a molecular expression for the friction constant that appears in the Fokker-Planck equation in momentum space, Green found molecular expressions for the various coefficients appearing in the Fokker-Planck equation in  $a$ -space. Starting from the Fokker-Planck equation, Green showed how the average behavior of the gross variables obeyed laws having exactly the same structure as the experimentally known transport laws. The transport laws obtained theoretically contain the coefficients that appear in the Fokker-Planck equation; by comparison, Green identified these coefficients with the various experimental transport coefficients.

By following the procedure just outlined, Green obtained expressions involving time-correlation functions for the coefficients of shear and bulk viscosity, thermal conductivity, diffusion, and thermal diffusion.

Other versions of this theory, extensions, and related material may be found in the book by DeGroot & Mazur (28), and in articles by Hashitsume (29), Lax (30), Onsager & Machlup (31), Uhlhorn (32), Van Kampen (33), and Yamamoto (34).

Green's theory is based on a number of assumptions, notably that the dynamical process of interest is a Markov process, and that the departure from thermal equilibrium is small. A rigorous justification of this theory, and an extension to non-Markoffian and nonlinear processes, has been given by Zwanzig (35). The quantum mechanical version of Zwanzig's theory was worked out recently by Sewell (36). Also, Mori (37) has obtained a "generalized Langevin" counterpart to the generalized Fokker-Planck theory.

At this point we must mention work bearing a strong family relation to the Fokker-Planck theory. Helfand (38) used a generalization of the Einstein formula  $\langle R^2 \rangle = 6Dt$  to derive expressions for other transport coefficients, along the same lines as the argument we just presented for the coefficient of diffusion of a Brownian particle. In their textbooks, Landau & Lifshitz (39) presented a theory of fluctuations in electrodynamic and hydrodynamic systems that may be regarded as the "Langevin equation" counterpart to Green's Fokker-Planck theory.

The third method used to establish connections between transport coefficients and time-correlation functions is based on Onsager's hypothesis concerning the regression of fluctuations (40). For further discussion of this hypothesis and its use in other connections see Casimir (41), DeGroot & Mazur (28), and Wigner (42).

Onsager's hypothesis asserts that spontaneous fluctuations from thermal equilibrium decay, on the average, according to the transport laws governing the corresponding macroscopic variables. (Because deviations from the average are of the same order of magnitude as the average itself, this assertion says nothing at all about the time dependence of a spontaneous fluctuation in any individual case. Only the average is supposed to behave in a systematic way.)

Kubo, Yokota & Nakajima (43) based a derivation of formulas for thermal transport coefficients on this hypothesis. The possibility of doing so is suggested clearly (at least by hindsight!) in Onsager's work; he demonstrated the symmetry of the matrix of transport coefficients in coupled irreversible processes, i.e., the reciprocal relations. But in order to give a statistical mechanical treatment of some property of transport coefficients, one must have some kind of representation of the transport coefficients. Kubo, Yokota & Nakajima extracted the appropriate representation from Onsager's ideas.

To illustrate how the method works, we consider here the simplest example, where the macroscopic transport law concerns only the average value  $\bar{a}(t)$  of a single dynamical quantity  $a(t)$ ,

$$\frac{d\bar{a}(t)}{dt} = -M\bar{a}(t)$$

Thus  $M$  is a rate constant, or transport coefficient, for the decay of  $\bar{a}(t)$ . The quantity  $a$  is chosen so that its average value vanishes at thermal equilibrium.

The transport law describes an average behavior; but in any actual experiment, one follows the evolution of a particular system and a particular quantity  $a(t)$ . If experiments are repeated in a macroscopically reproducible way, the initial values  $a(0)$  will be the same in each repetition. Later values  $a(t)$  will differ slightly as a result of uncontrolled differences between initial states on the molecular level. The average  $\bar{a}(t)$  in repeated experiments depends parametrically on the initial value  $a(0)$  common to all repetitions.

The observation just made is put to use in this theory in the following way. Let us multiply both sides of the transport law by the initial value  $a(0)$ , and then average over an equilibrium ensemble of initial values, denoted by  $\langle \rangle$ :

$$\left\langle \frac{d}{dt} \bar{a}(t)a(0) \right\rangle = -M\langle \bar{a}(t)a(0) \rangle$$

The resulting equation now contains a double average: first a conditional average over repetitions for the given  $a(0)$ , and then an unconditional average over the equilibrium distribution of  $a(0)$ . Evidently the same average can be computed more directly. If  $A(t)$  is the numerical value of a function  $A(p(t), q(t))$  in phase space, then we may write the double average in the form of a time-correlation function,

$$\begin{aligned} \langle \bar{a}(t)a(0) \rangle &= \langle A(p(t), q(t))A(p(0), q(0)) \rangle \\ &= \langle A(t)A(0) \rangle \end{aligned}$$

(It is perhaps easiest to verify this by working backwards from the right hand side.)

The regression hypothesis has just been used without being stated explicitly. The point is that when we average over an equilibrium distribution of initial  $a(0)$ , the major contribution comes from very small values of  $a(0)$ , of the order of spontaneous fluctuations. But then we want the transport law to be valid for such small initial values. This is precisely what the regression hypothesis is about.

As a result of the preceding manipulations, the transport law now has the form

$$\langle \dot{A}(t)A(0) \rangle = -M\langle A(t)A(0) \rangle$$

Let us integrate this equation over a small time interval  $t$ ,

$$\int_0^t dt' \langle \dot{A}(t')A(0) \rangle = -M \int_0^t dt' \langle A(t')A(0) \rangle$$

If  $Mt$  is much smaller than unity, the right hand side can be simplified to

$$= -tM\langle A(0)A(0) \rangle + O(M^2t^2)$$

We assume that  $t$  is always small enough for this approximation to be good. On the left, we take advantage of time invariance to shift the time origin,

$$\langle \dot{A}(t') A(0) \rangle = \langle \dot{A}(0) A(-t') \rangle$$

and then we introduce another time derivative by

$$A(-t') = A(0) - \int_0^{t'} ds \dot{A}(-s)$$

This gives, for small enough  $t$ ,

$$\int_0^t dt' \langle \dot{A}(0) A(0) \rangle - \int_0^t dt' \int_0^{t'} ds \langle \dot{A}(0) \dot{A}(-s) \rangle = -tM \langle A(0) A(0) \rangle$$

The first term on the left vanishes because

$$\langle \dot{A} A \rangle = \left\langle \frac{1}{2} \frac{d}{dt} A^2 \right\rangle$$

and because the equilibrium average of a rate of change must vanish. In the second term on the left, the time origin is shifted back by an interval  $s$ ; this replaces  $\langle \dot{A}(0) \dot{A}(-s) \rangle$  by  $\langle \dot{A}(s) \dot{A}(0) \rangle$ . Finally, the order of integration is reversed, the  $t'$  integration is performed immediately, and both sides of the equation are divided by  $t$ , yielding

$$\int_0^t ds (1 - s/t) \langle \dot{A}(s) \dot{A}(0) \rangle = M \langle A^2 \rangle$$

This equation is very much like one already encountered in this review, and it is handled in the same way. Again, the decisive question is whether the time-correlation function decays fast enough. If it does, then we may drop the extra term  $s/t$  in the integrand, and replace the upper limit  $t$  by any time  $\tau$  long enough for the integrand to have decayed to zero. In this case, we get

$$M = \int_0^\tau ds \langle \dot{A}(s) \dot{A}(0) \rangle / \langle A^2 \rangle$$

The rate constant is now expressed by means of a time-correlation function in the time derivative of the quantity of interest.

The result of the derivation does not look quite like the earlier formulas for transport coefficients, because of the extra factor  $\langle A^2 \rangle$ . The difference can be understood, however, by remembering that transport coefficients are usually defined as coefficients describing the response  $J = da/dt$  to a thermodynamic force  $\mathcal{F}$ ,

$$J = L\mathcal{F}$$

The force is the derivative of a nonequilibrium entropy  $S(a)$  with respect to a deviation from equilibrium,

$$\mathcal{F} = \frac{\partial S(a)}{\partial a}$$

The entropy, being a maximum at equilibrium, can be expanded in powers of  $a$ ,

$$S(a) = S(0) - \frac{1}{2}ga^2 + \dots$$

so that the transport law takes the form

$$J = -Lg\bar{a}$$

The quantity  $Lg$  corresponds to  $M$ . By means of equilibrium fluctuation theory (28), it is easy to show that

$$\langle A^2 \rangle = k_B g^{-1}$$

Then the transport coefficient  $L$  has the same structure as our earlier formulas,

$$L = \frac{1}{k_B} \int_0^\tau ds \langle \dot{A}(s) \dot{A}(0) \rangle$$

Along with the regression hypothesis, this theory involves another assumption. It is supposed to be possible to find a time  $\tau$  that is long enough for the time-correlation function to decay to zero, but also short enough to fulfill the condition that  $M\tau$  be much smaller than unity.

Kubo, Yokota & Nakajima (43), and also Kubo (7), have given plausible arguments that this assumption is safe. A more rigorous analysis by Zwanzig (44) led to the conclusion that the theory is valid whenever the transport process under consideration is "slow enough" in a mathematically well-defined sense. Thus the theory may be applied, e.g., to ordinary hydrodynamic processes, but perhaps not to extremely fast chemical reactions in shock waves. (This remark is conjectural—no numerical estimates have been made.)

The basic assumption of the theory, the regression hypothesis, can be justified only in the context of a more general theory. Van Kampen (33) has shown that it is correct in the context of the Fokker-Planck theory, at least for linear transport laws. In fact, the regression hypothesis is no more than a statement that transport laws linear for macroscopic departures from equilibrium are still linear, and with the same slopes, for microscopic departures from equilibrium. Any exception to this would be astonishing indeed.

The fourth method used to relate transport coefficients to time-correlation functions was invented in 1956 by Mori (15, 45); we call this the local equilibrium theory. Recently Longuet-Higgins (46) has presented a simple and pedagogically useful version of this theory.

The basis of this method is the observation that when a typical non-equilibrium system relaxes toward thermal equilibrium, it passes through a sequence of local equilibrium states. Consider, e.g., thermal conduction in a temperature gradient. Use of the notion of a temperature gradient implies that the nonequilibrium system can be described by a local temperature. But this in turn implies that the system can be treated as if it were locally canonical.

Andersen et al. (47) have discussed a class of systems for which relaxa-

tion proceeds through a sequence of Boltzmann distributions, as assumed in the local equilibrium theory. Their results, while exact, are based on treatment of dynamics as a Markoff process; and this is generally not correct except in certain special limiting cases.

As a very simple illustration of the local equilibrium theory, we consider the case where only a single macroscopic variable  $A$  (aside from the total energy  $H$ ) is of interest. The ensemble mean values of these quantities are denoted by  $\bar{A}$  and  $\bar{H}$ . In an equilibrium ensemble where  $\bar{A}$  is held fixed by some kind of external constraint, the phase space distribution function  $f(p, q)$  is

$$f(p, q) = Q^{-1} \exp(-\beta H - \gamma A)$$

The normalizing factor is the partition function  $Q(\beta, \gamma)$ ,

$$Q(\beta, \gamma) = \int \int d\mathbf{p} d\mathbf{q} \exp(-\beta H - \gamma A)$$

This distribution function gives maximum entropy under the constraints of fixed  $\bar{H}$  and  $\bar{A}$ . The normal thermal equilibrium distribution function, appropriate when  $\bar{A}$  is not constrained, is obtained by setting  $\gamma$  equal to 0. Thermal equilibrium mean values, with  $\gamma=0$ , will be denoted as in the previous discussion by angular brackets  $\langle \rangle$ . The functional relation between the Lagrange multipliers  $\beta$  and  $\gamma$ , and the mean values  $\bar{H}$  and  $\bar{A}$ , is given by the well known formulas

$$\bar{H} = -\frac{\partial \log Q}{\partial \beta}, \quad \bar{A} = -\frac{\partial \log Q}{\partial \gamma}$$

The principal assumption of the local equilibrium theory is that the phase space distribution function maintains the above form for all times; the relaxation toward equilibrium due to removing the constraint fixing  $\bar{A}$  is supposed to be described by a time-dependent coefficient  $\gamma(t)$ . The other coefficient  $\beta$  is independent of time because  $H$  is a constant of the motion.

This assumption is demonstrably not correct, except for the trivial case where  $A$  is also a constant of the motion. It has the further failing, that the mean value of the rate of change of  $A$  invariably vanishes. Very likely, however, the true distribution function of a relaxing system does not deviate appreciably from the locally canonical form, because the idea of local thermal equilibrium in a relaxing system appears to be experimentally justified.

In practice, the locally canonical distribution is used as follows. It is assumed to be correct at some initial time  $t=0$ . Then the system is allowed to “age” for a certain time interval  $\tau$ . This time is supposed to be long enough for many dynamical processes (e.g., collisions between molecules) to occur, but still short enough that the macroscopic state of the system has not changed appreciably. Finally, the mean value of the current  $J=\dot{A}$  is measured at  $\tau$ . This average is given explicitly by

$$\bar{J}(\tau) = Q^{-1} \int \int d\mathbf{p} d\mathbf{q} \dot{A}(\tau) \exp(-\beta H - \gamma A)$$

Small deviations from equilibrium correspond to small  $\gamma$ . In fact, the thermodynamic force associated with the variable  $A$  can be shown to be just

$$\mathcal{F} = k_B \gamma + O(\gamma^2)$$

This suggests an expansion of the average current in powers of  $\gamma$ , giving

$$\bar{J}(\tau) = \langle J(\tau) \rangle - \gamma \langle \dot{A}(\tau) A(0) \rangle + \gamma \langle J(\tau) \rangle \langle A(0) \rangle + O(\gamma^2)$$

It should be recalled that  $\bar{J}$  is the current in the nonequilibrium ensemble, while  $\langle J \rangle$  is the current at thermal equilibrium. The latter quantity vanishes, so that

$$\bar{J}(\tau) = -\gamma \langle \dot{A}(\tau) A(0) \rangle + O(\gamma^2)$$

By performing manipulations exactly like those already described in connection with the method based on the regression hypothesis, this may be transformed without further approximation into

$$\bar{J}(\tau) = L \mathcal{F}(0)$$

The transport coefficient  $L$  is given by the same formula already obtained using the other approaches,

$$L = \frac{1}{k_B} \int_0^\tau ds \langle \dot{A}(s) \dot{A}(0) \rangle$$

By the assumption that  $\tau$  is a macroscopically short time, the thermodynamic force at  $t=0$  will hardly differ from its value at  $t=\tau$ , so that both sides of the transport law can be expressed as functions of the same time  $\tau$ ,

$$\bar{J}(\tau) = L \mathcal{F}(\tau)$$

But if the phase space distribution function is locally canonical to a good approximation, then the result just obtained is independent of the choice of origin in time and is generally valid.

We shall not go into the various arguments that may be used to justify the preceding derivation. It may be of some interest, however, to notice the relation of the local equilibrium theory to the rigorous generalization of the Fokker-Planck theory set forth by Zwanzig (35). The idea behind this work was the separation of the phase space distribution function into a "relevant" part and an "irrelevant" part by means of a projection operator. The relevant part was chosen to be microcanonical in the gross variables; as is well known, there is usually no practical distinction between the microcanonical and canonical ensembles, so that the relevant part corresponds to Mori's locally canonical distribution. Then an exact kinetic equation was derived for the relevant part—this was put into the form of a generalized Fokker-Planck equation, but it could have been left just as well in the form of a kinetic equation in phase space. The effects of the "aging" process were accounted for in the time dependence of the irrelevant part of the distribution. This appeared at an intermediate step in the derivation of the kinetic equation for the relevant part.

The theoretical treatments of transport phenomena that we have just

discussed all fall into two general categories, response to an externally imposed force, or free relaxation toward equilibrium. One important kind of irreversible behavior is not accounted for by these treatments: response to interaction with a heat bath. This gap is filled by the external reservoir theory.

The original intention of the external reservoir theory was to provide an obvious mechanism for the approach of a nonequilibrium system toward thermal equilibrium. This was accomplished by coupling the system to a heat bath or reservoir, in such a way that the interaction is a random process. The heat bath is supposed to be so large that it always stays in thermal equilibrium, no matter what the system is doing. In this connection, the principal references are a series of articles by Bergmann & Lebowitz (48–51).

It was then realized that external reservoirs could be used to maintain a system in a steady nonequilibrium state. For example, a steady temperature gradient could be set up by connecting the system to two reservoirs having different temperatures. By determining the various currents in this steady state, one then finds formulas for transport coefficients, e.g., thermal conductivity.

This program has been carried out particularly by McLennan (17, 52, 53). His review article provides an excellent summary of this work (54), so we shall not present any detail here. The results are the same as obtained by the other methods, so that one has learned at least that transport coefficients are independent of the method used to establish a departure from equilibrium.

Other articles covering much the same ground have been published by Kirkwood & Fitts (55), Lebowitz & Shimony (56), Bernard (57), and Lax (30).

The final method for treating irreversible processes to be discussed in this part of the review is the prediction theory due to Jaynes & Scalapino (58). This theory is an extension to time-dependent phenomena of Jaynes' earlier work (59) on the relation of information theory to statistical thermodynamics.

The gist of Jaynes' method is as follows. Suppose we know certain properties of a many-body system, e.g., its average energy and perhaps the averages of some other quantities  $A$ . How can we predict other properties of the same system? The answer, of course, has been known for a long time: we construct a canonical ensemble out of the specified mean values, and then we use the distribution function of this ensemble to calculate mean values of the other quantities. Jaynes pointed out that this familiar procedure may be regarded as an application of information theory, simply by using the Gibbs entropy of an ensemble as a measure of the amount of information one has about that ensemble. The "best" ensemble corresponding to given information about the system (in the form of mean values) is the one that describes this information without assuming any extra information—or it is the one having maximum Gibbs entropy consistent with the given information.

Jaynes proposed that nonequilibrium processes be treated in just the same way. Suppose that we know the history of certain mean values over some specified time interval. Then by maximizing the Gibbs entropy of the ensemble corresponding to this given information, we can construct a generalized canonical ensemble. This ensemble gives exactly the specified mean values, at least over the specified time interval. (The ensemble distribution function bears a very strong resemblance to Mori's local equilibrium distribution, although its source is different.)

But now we can use this generalized canonical ensemble to predict the future behavior of the system. For example, a heat current may have flowed steadily during the period of observation. The ensemble distribution function contains information about this current, in the form of a time-dependent Lagrange multiplier arising from the variational problem of maximizing entropy under the constraint of specified mean heat current. This Lagrange multiplier clearly involves the temperature gradient associated with the heat current. Now we calculate the "free," i.e. the unconstrained, future behavior of the heat current. In the first approximation, the unconstrained heat current turns out to be proportional to the temperature gradient; from the coefficient of proportionality, we get the thermal conductivity. The results of this and related calculations are in exact agreement with those obtained by other methods.

This concludes our review of six methods used to relate transport coefficients to time-correlation functions. Before turning to the next topic, however, we wish to express a few opinions as to the general inter-relations of these methods.

The indirect Kubo method appears to be the simplest and most direct. Its application is limited to those cases where we already know the structure of the relevant transport law, e.g., the Navier-Stokes equation. Further, we must also know how an externally imposed force (even though fictitious) will affect the motion of the system. As new and unfamiliar problems come up, this method may lose its attractiveness. For an example of a somewhat dubious application, consider the calculation of a reaction rate. With few exceptions, the structure of the transport laws of chemical kinetics is not known (because of the extremely complicated nature of most chemical reactions). Another somewhat similar example is in rheology, where there is still considerable argument as to how to take account of various kinds of non-Newtonian behavior.

The preceding remarks apply also to the method based on the regression hypothesis.

The Fokker-Planck theory (in the original form attributed to Green) and the local equilibrium theory of Mori are restricted to the treatment of only the low frequency parts of transport coefficients. While this does not exclude the usual hydrodynamic applications, it does exclude applications to certain interesting processes involving "memory effects," e.g., various rheological phenomena.

This restriction was removed in Zwanzig's generalized Fokker-Planck theory. This theory, however, is rather complicated and abstract; and no applications have been made so far.

As mentioned already, the results obtained by various authors differ in appearance also because of the use of different ensembles. In our opinion the most satisfactory explanation of the apparent difference, and the actual equivalence, is that of McLennan (19).

We have remarked several times that these methods all lead to the same results. This assertion must be qualified slightly. Some methods lead automatically to expressions for transport coefficients that involve integrations over a characteristic time interval  $\tau$ , long compared with molecular times, and short compared with macroscopic times. Other methods (in my opinion more rigorous) lead to integrals over an infinite time interval, coupled usually with some limiting process (for example, to zero frequency). In a practical sense these two kinds of results should be regarded as identical, although they differ in formal appearance.

#### APPLICATIONS OF TIME-CORRELATION FUNCTIONS

*Friction constant.*—The frictional force on a Brownian motion particle (or B-particle) is  $-\zeta v$ , where  $v$  is the velocity of the particle and  $\zeta$  is the friction constant. Kirkwood (25) was the first to derive a statistical mechanical expression for  $\zeta$ ,

$$\zeta = \frac{1}{3} \beta \int_0^\tau dt \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle$$

The total force exerted on the B-particle by its surroundings at time  $t$  is  $\mathbf{F}(t)$ . The derivation of this formula lacks rigor; in distinction to the other transport coefficients to be discussed here, there is some question as to the general correctness of Kirkwood's result.

Many calculations of  $\zeta$ , particularly for liquid argon, have been presented. An early one, typical of several others, was given by Kirkwood, Buff & Green (60) in connection with their theory of viscosity. Their calculation was based on the assumption that the time-correlation function decays exponentially,

$$\langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle = \langle \mathbf{F}(0) \cdot \mathbf{F}(0) \rangle \exp(-\lambda t)$$

so that the time integral can be found immediately. They made the further assumption that  $1/\lambda$ , a natural time associated with Brownian motion, could be identified with the momentum relaxation time  $m/\zeta$ . This leads directly to

$$\zeta^2 = \frac{1}{3} \beta m \langle \mathbf{F}^2 \rangle = \frac{1}{3} m \langle \nabla^2 U \rangle$$

The second form is obtained by integration by parts;  $U$  is the total intermolecular potential felt by the B-particle.

The same formula was obtained, by a somewhat different argument, by Rice & Kirkwood (61). Their approach was based on the idea of diffusion in

the space of a pair of particles. The pair force between molecules  $i$  and  $j$  at time  $t$  may be expressed as a function of the relative separation  $R_{ij}(t)$ . These authors treated the change in  $R_{ij}$  during the time interval  $\tau$  as small compared with typical intermolecular separations; they used a generalization of Einstein's Brownian motion equation for the mean squared separation during  $\tau$ ,

$$\langle \Delta R_{ij}(\tau) \Delta R_{ij}(\tau) \rangle = D^{(2)}\tau$$

and they treated  $D^{(2)}$ , the diffusion tensor in pair space, as a direct sum of diffusion tensors in the spaces of the individual molecules. Finally, they related  $D$  to  $\xi$  by the familiar expression  $D = k_B T / \xi$ .

Incidentally, it should be noted that the latter equation, which is valid for Brownian motion of a large particle in a bath of small particles, is probably not valid otherwise. For a discussion of the validity of formulas of this type, see Balescu (62), Swenson (63), and Zwanzig (64).

Several articles in Kirkwood's series on transport processes (65, 66) made use of a friction constant calculated in the linear trajectory approximation. Only the result of the approximation was given in these articles; the general theory, and some extensions, was discussed later by Helfand (67). In essence, the approximation consists of calculating the force  $F(t)$  on the B-particle as if the particle were moving in a straight line, unaffected by interactions with the environment. This approximation is in fact exact in the limit of weak interactions between particles, as shown first by Ross (68). It does not appear to be particularly sensible for dense gases or liquids, so modifications have been made to take account of hard core repulsions as well as weak attractions; see Rice & Allnatt (69) and Helfand (67).

We mention finally a curious acoustical model, in which the environment is treated as a hydrodynamic continuum. The mechanism of friction is radiation damping associated with the emission of sound waves. This approach was investigated by Fixman (70), Kotin (71), and Rice (72). Rice's article contains a good summary of the relations between various methods.

The friction constant has a special and annoying property not possessed by the other transport coefficients to be discussed here; the cutoff time  $\tau$  cannot safely be replaced by infinity. If this is done, the whole integral vanishes. This peculiarity has been discussed by Suddaby & Gray (73), Helfand (67), and Zwanzig (44). Its main consequence is that physical intuition has to be used in the choice of  $\tau$ . This is an important reason for doubting the general exactness of Kirkwood's theory.

There are, however, some exceptions. If the decay of the time-correlation function of momentum is governed by some parameter of slowness  $\epsilon$ , then the corresponding friction constant is given exactly by

$$\xi = \frac{1}{3} \beta \int_0^\infty dt \lim_{\epsilon \rightarrow 0} \langle F(0) \cdot F(t) \rangle$$

This formula applies in particular in the limit when the B-particle interacts

weakly with its environment, so that  $\epsilon$  is the interaction strength. In this case one obtains the linear trajectory result. It applies also when the B-particle is very much heavier than the surrounding molecules, so that  $\epsilon$  is the mass ratio. These exact results were first obtained by Lebowitz & Rubin (27), and later by Zwanzig (44); they constitute the only rigorous formulas available for friction constants.

In the heavy mass limit, which might be termed "real" Brownian motion,  $\zeta$  has been calculated explicitly in two extreme limits. Green (74), Mazo (75), and Andersen & Shuler (117) have treated the "Rayleigh" gas, where the mean free path of the molecules in the environment is much greater than the radius of the B-particle. In another extreme, the environment is a dense fluid treated as a hydrodynamic continuum undergoing fluctuations. The friction constant for this case, calculated by Zwanzig (76), is exactly as given by Stokes' law.

Kirkwood's theory of the friction constant for translational motion has its analogue for rotations. This topic has been treated by Steele (77).

*Viscosity.*—Formulas for the coefficients of shear viscosity  $\eta$  and bulk viscosity  $\eta_v$  were obtained first by Green (12) by means of the Fokker-Planck theory. Thereafter, the same results were found by most of the other procedures outlined in the previous section. We pass by a certain amount of controversy about the agreement between results obtained by different methods, which has now been settled, and present only the final results.

Time-correlation function expressions for shear and bulk viscosity, in classical mechanics, are given by

$$\begin{aligned}\eta &= \frac{1}{V} \beta \int_0^\infty dt \langle J^{ab}(0) J^{ab}(t) \rangle \\ \eta_v &= \frac{1}{V} \beta \int_0^\infty dt \frac{1}{9} \sum_a \sum_b \langle J^{aa}(0) J^{bb}(t) \rangle\end{aligned}$$

Here  $V$  is the volume of the system. The tensor  $J^{ab}$ , (for  $a, b = 1, 2, 3$ ), is

$$J^{ab} = \sum_i \frac{\dot{p}_{ia} \dot{p}_{ib}}{m_i} + \sum_i R_{ia} F_{ib} - \langle J^{ab} \rangle$$

The  $a$ -th cartesian component of the position of the  $j$ -th molecule is  $R_{ja}$ ; the corresponding component of momentum is  $p_{ja}$ ; the  $a$ -th component of total force on the  $j$ -th molecule is  $F_{ja}$ ; the mass of this molecule is  $m_j$ ; and the subtracted part  $\langle J^{ab} \rangle$  is a function of pressure  $\bar{P}$ , internal energy  $E$ , and particle number  $N$ ,

$$\langle J^{ab} \rangle = V \delta_{ab} \left\{ \bar{P} + \frac{\partial \bar{P}}{\partial N} (N - \langle N \rangle) + \frac{\partial \bar{P}}{\partial E} (E - \langle E \rangle) \right\}$$

This subtracted part, needed only for the bulk viscosity, takes account of the ensemble used for the averages. For example, if we use the microcanonical ensemble, then  $N = \langle N \rangle$  and  $E = \langle E \rangle$ , so two terms drop out. With the canonical ensemble, the energy difference does not vanish, while with the grand canonical ensemble, both terms are present.

The first treatment of thermal transport coefficients by means of time-correlation functions appears in a virtually unnoticed article by Herzfeld (78) in 1958. His approach is based on the assumption that the time-correlation function decays exponentially. As in the example of the friction constant that we have already discussed, this assumption relates the transport coefficient to a relaxation time and to an equilibrium fluctuation. Herzfeld did not provide any theoretical discussion of the relaxation time. In calculating the equilibrium fluctuation, he made several approximations, e.g., neglect of certain correlations in space. For the shear viscosity, he obtained finally an expression very much like the one obtained by Eyring using the transition state theory. While Herzfeld's theory is not conclusive, it is very attractive and deserves further investigation.

Several authors have discussed the equivalence of the time-correlation function method and the more familiar Boltzmann equation method for calculating the viscosity of gases at low densities: Mori (79), Fujita (80), and McLennan & Swenson (81). It turns out that in evaluating the time-correlation function, one finds at an intermediate stage that one has to solve a certain integral equation. This equation is identical with an equation appearing in the first Chapman-Enskog solution of the Boltzmann equation; it is the equation that has been used many times to calculate the viscosity of low density gases, and the results are known to be in excellent agreement with experiment.

To go to the next order in density, one must take proper account of triple collisions. Approximate calculations based on time-correlation functions have been reported by Ono & Shizume (82) and Wainwright (83). An exact treatment was given by Kawasaki & Oppenheim (84). Their calculation was based on a generalization of a procedure used by Zwanzig (85) to discuss self-diffusion in gases. The main result obtained by Kawasaki & Oppenheim, as in the two-body case, was that a certain integral equation appeared at an intermediate stage. This equation is a generalization of the Chapman-Enskog equation to the next order in density. The same equation is obtained from solution of the generalized Boltzmann equation derived by Choh & Uhlenbeck (86). The equation contains a kernel, analogous to the collision cross section for binary interactions, but containing also three body interactions. As yet no one has calculated this kernel, so that no numerical results have been obtained.

Ernst (118) has recently presented a somewhat different demonstration of the equivalence of the time-correlation approach and the generalized Boltzmann equation approach.

*Thermal conductivity.*—The coefficient of thermal conductivity, in classical mechanics, is

$$\kappa = \frac{1}{3Vk_B T^2} \int_0^\infty dt \langle \mathbf{S}(0) \cdot \mathbf{S}(t) \rangle$$

The "heat current"  $\mathbf{S}$  appearing here is given most conveniently in the form

$$\mathbf{S} = \frac{d}{dt} \sum_i (H_i - h_i) \mathbf{R}_i$$

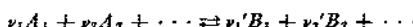
where  $H_j$  is the contribution of the  $j$ -th molecule to the total Hamiltonian of the system, and  $h_j$  is the enthalpy per molecule. (The potential energy of interaction of pairs of molecules is divided equally between partners.)

References given in the discussion of viscosity, concerned with the question of density expansions, are equally relevant to the theory of thermal conductivity of gases. For example, it is known that the above formula gives results identical with the conventional Boltzmann equation approach, in the binary collision regime.

Considerable attention has been devoted to the use of time-correlation function methods in calculating thermal conductivity of crystal lattices (due to anharmonic phonon-phonon scattering or impurity scattering). We shall not discuss this work here, but merely mention some names: Hardy (87), Schieve & Peterson (88), and Maradudin (89).

A characteristic property of metals is expressed in the Wiedemann-Franz law, which relates the thermal conductivity of a metal to its electric conductivity. In a beautiful application of time-correlation function methods, Chester & Thellung (90) have shown that this law is an exact consequence of the one-electron theory of metals.

*Chemical reaction rates.*—Consider a chemical reaction of the form



The stoichiometric coefficients  $\nu_i$  of the reactants are taken to be positive, and the  $\nu'_i$  (with primes) of the products are taken to be negative. Let  $N_1, N_2, \dots$  and  $M_1, M_2, \dots$  be the number of molecules of reactants and products present in the mixture; and use  $\Delta N_j$  and  $\Delta M_j$  for deviations from thermal equilibrium values. Because of the structure of the rate equation, the various changes in composition are all related by

$$\frac{\Delta N_1}{\nu_1} = \frac{\Delta N_2}{\nu_2} = \dots = \frac{\Delta M_1}{\nu'_1} = \frac{\Delta M_2}{\nu'_2} = \dots = \Delta N$$

which defines  $\Delta N$ . Thus we may use the single variable  $\Delta N$  to describe the extent to which the reaction has taken place at any time.

The thermodynamic driving force for the reaction is the chemical affinity  $\mathfrak{G}$ ,

$$\mathfrak{G} = - \sum \nu_i \mu_i - \sum \nu'_j \mu'_j$$

where  $\mu$  and  $\mu'$  are the chemical potentials of the reactants and products. For small departures from equilibrium, the rate of the reaction is expressed (in the characteristic Onsager form of irreversible thermodynamics) as

$$\frac{d\langle \Delta N \rangle}{dt} = G\mathfrak{G}$$

The rate is a constant times the driving force. Then  $G$  is the rate constant of the reaction. (The forward and reverse rates can be obtained from knowledge of  $G$  and of the equilibrium constant of the reaction.)

Having written the rate equation in the standard form, it is easy to see that  $G$  is given by

$$G = \beta \int_0^{\infty} dt \langle \dot{N}(0) \dot{N}(t) \rangle$$

The rate constant is determined by the time-correlation function of the instantaneous time derivative  $dN/dt$ .

This result was derived first by Yamamoto (91). A later review by Aroeste (92) contains a similar treatment.

Up to now, the only progress made along these lines has been the demonstration that the time-correlation function can be calculated in terms of reaction cross sections at low density, leading to results known from more intuitive arguments (91, 92).

*Nuclear magnetic resonance.*—The earliest, and most fruitful, application of time-correlation function techniques to problems of irreversible behavior were made in connection with NMR line shapes. The basic formula is due to Kubo & Tomita (13). Let  $\chi_{\mu\nu}(\omega)$  be the frequency dependent magnetic susceptibility tensor of a material, let  $M$  be the total magnetic moment of the system, and let  $V$  be its volume. Then  $\chi$  is expressed by means of the time-correlation function of the rates of change of magnetic moments by

$$\chi_{\mu\nu}(\omega) = \frac{\beta}{i\omega V} \int_0^{\infty} dt e^{-i\omega t} \langle \dot{M}_\nu(0) \dot{M}_\mu(t) \rangle$$

An alternative form, obtained by integrating by parts, is

$$\chi_{\mu\nu}(\omega) = \frac{\beta}{V} \langle \dot{M}_\nu M_\mu \rangle - \frac{\beta i\omega}{V} \int_0^{\infty} dt e^{-i\omega t} \langle \dot{M}_\nu(0) M_\mu(t) \rangle$$

This contains  $M$  instead of  $dM/dt$ , and shows clearly the relation of  $\chi(\omega)$  to the familiar static result.

The substantial literature dealing with applications of this formula is reviewed regularly, in these volumes and elsewhere: so we just mention here a few articles that appear to have special interest.

Argyres & Kelley (93) have recently given a thorough and general analysis of the theory of resonance and relaxation in spin systems, using modern quantum statistical mechanical methods.

Oppenheim, Bloom & Torrey (94–96) developed a theory of nuclear spin-lattice relaxation times in gases and liquids. An interesting feature of this work is the use of a “constant acceleration approximation” in the calculation of time-correlation functions. (From their point of view, the linear trajectory approximation that we referred to earlier may be termed a “constant velocity approximation.”)

*Electric conductivity.*—The time-correlation function formula for the

electric conductivity tensor  $\sigma_{\mu\nu}(\omega)$  is

$$\sigma_{\mu\nu}(\omega) = \frac{\beta}{V} \int_0^\infty dt e^{-i\omega t} \langle \mathbf{J}_\nu(0) \mathbf{J}_\mu(t) \rangle$$

where  $\mathbf{J}$  is the total electric current density in the system. This formula was given by Kubo in 1957.

Many calculations of  $\sigma$  have been based on Kubo's formula. Most of this effort has been directed at the electric conductivity of metals; see, in particular, articles by Montroll & Ward (97), Berger, Van Leuwen & Verboven (98), and Janner (99). We do not comment on this work, except to note that as usual, the results agree with those obtained by more elementary methods in the limiting cases where elementary methods apply (e.g., low density of scattering impurities).

Of considerable interest to physical chemists is a treatment of electric conductivity of ionic solutions, due to Friedman (100). He obtained a cluster expansion of the above formula for  $\sigma$ , modeled on an expansion found earlier by Montroll & Ward (97). This approach, while not yet thoroughly explored, is likely to lead to a much more detailed molecular picture of ionic conductivity than any other theory presently available.

**Dielectric susceptibility.**—In applying Kubo's method to the calculation of dielectric susceptibility, a special problem comes up, associated with the long range character of dipolar forces. This problem is familiar in the theory of the static dielectric constant, and is discussed fully, for example, in Fröhlich's book (101).

The difficulty can be put as follows. The most natural way to apply Kubo's method is to impose an electric field on a macroscopic body, and to then determine its total induced electric moment. The ratio of these quantities is called the net polarizability of the body. But, as is well known, the net polarizability does not depend only on the dielectric susceptibility of the material, but also on the shape of the body. For this reason, if one wants a time-correlation function theory of dielectric susceptibility, one must specify the shape of the body for which the time-correlation function is to be calculated.

Consider a spherical specimen of the material of interest, and, for simplicity, consider only an isotropic material, so that the dielectric susceptibility  $\epsilon(\omega)$  is a scalar quantity. The net polarizability  $\alpha_s(\omega)$  of the sphere is related to  $\epsilon$  by

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{4\pi}{3} \alpha_s(\omega)$$

Kubo's method gives for  $\alpha_s$  the formula

$$\alpha_s(\omega) = \frac{\beta}{3V} \langle M^2 \rangle - \frac{\beta i\omega}{3V} \int_0^\infty dt e^{-i\omega t} \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle$$

where  $M$  is the total instantaneous electric moment of the sphere. (The

resemblance of this formula to one given previously for magnetic susceptibility will be evident.) The preceding equation appears to have been given first by Glarum (102).

Glarum's article contains also an interesting discussion of the relation between macroscopic decay times (i.e., those associated with the decay of macroscopic polarization) and microscopic relaxation times (i.e., those associated with such molecular processes as re-orientation of individual molecules).

Starting with the above formula for  $\epsilon(\omega)$ , Zwanzig (103) investigated the effects of dipolar interactions on the relaxation process. He considered, as a model, a rigid lattice of permanent point dipoles, undergoing isotropic Brownian motion (as in Debye's theory of dielectric relaxation). The calculation took account of the torques exerted on dipoles as a result of interactions with electric fields due to other dipoles. It was found that as soon as one observed deviations from ideal Debye-Langevin behavior of the static dielectric constant, one observed also deviations from ideal Debye relaxation.

In 1956, Fano (104) presented a quantum mechanical theory of dielectric behavior in dense media. He obtained some very interesting and significant results concerning the relation of  $\epsilon$  to the time-correlation function of the charge density. In particular, he observed that one gets either  $\epsilon$  or its reciprocal, depending on whether or not one includes certain long range electrostatic interactions in the Hamiltonian governing the time dependence of the time-correlation function. The same observation has been made, in a somewhat different context, by Ambegaokar & Kohn (105, 106).

The theory of pressure broadening, i.e., the effects of gas collisions on spectral line shapes, has been investigated by means of time-correlation functions by Fano (107). A technical feat of this work was the derivation of a relation between the scattering operator in the quantum mechanical Liouville representation and the corresponding scattering operator in the Schrodinger representation.

*Inelastic neutron scattering.*—The cross section for inelastic scattering of neutrons by macroscopic systems may be expressed in terms of time-correlation functions, as shown by Van Hove (108). We do not give all the details; in essence, the coherent part of the scattering, associated with momentum transfer  $\hbar q$  and energy transfer  $\hbar\omega$ , is proportional to

$$S_c(q, \omega) = \int \left\langle \sum_i e^{-iq \cdot R_i(0)} \sum_j e^{iq \cdot R_j(t)} \right\rangle e^{-i\omega t} dt$$

This is evidently the frequency spectrum of the  $q$ -th Fourier component of the local density of the material. The incoherent part of the scattering is proportional to

$$S_i(q, \omega) = \int \sum_l \langle e^{-iq \cdot R_l(0)} e^{iq \cdot R_l(t)} \rangle e^{-i\omega t} dt$$

Note that the cross terms ( $j \neq l$ ) present in  $S_c$  are omitted from  $S_i$ .

The extensive literature on these quantities has been reviewed many-

times, particularly in the proceedings of symposia organized by the International Atomic Energy Agency (109). For some recent advances in the detailed theoretical analysis of the above time-correlation functions, see articles by Nelkin & Ghatak (110), Yip & Nelkin (111), Nossal (112), Van Leeuwen & Yip (113), and Singwi (114).

The incoherent part of the scattering can be related to the time-correlation function of the current density of a particular molecule in the medium; by using this relation, Zwanzig (115) showed how  $S_i(q, \omega)$  is related to a generalized self-diffusion coefficient  $D(q, \omega)$ .

Rahman (116) solved the equations of motion of 864 argon atoms in a box, by means of high speed digital computers, under conditions appropriate to liquid argon. Among many interesting results, he calculated the time-correlation function of velocity and its frequency spectrum. These quantities differ substantially from previous expectations. Rahman's calculations provide what is probably the most detailed "experimental" information currently available about dynamical processes in liquids.

#### FUTURE DEVELOPMENTS

In the final part of this review, I make the dangerous attempt to predict some future developments in this field. To a large extent, the following predictions are described better as wishful thinking; these are some of the things that I would like to see worked out.

With respect to practical calculations of transport coefficients, little progress can be expected in the next few years. The easy problems were done long ago by other methods (e.g., viscosity of a gas at low density). The time-correlation function method provides a more rigorous basis for the older theory, but it adds little of practical value. Attempts are being made to evaluate the triple collision contribution to transport coefficients of gases, but the theory looks extremely hard. Even if it is successful, such calculations probably will not replace direct measurement as the most economical method of getting numbers.

There seems to be little question as to the correctness of time-correlation expressions for the standard transport coefficients. I expect that a fair amount of attention will be given to the rigorous treatment of transport processes involving nonlocal effects of the sort described by frequency and wave vector dispersion. Investigations of this type may help to bridge the gap between macroscopic hydrodynamics and molecular dynamics. That is, hydrodynamic processes at sufficiently high frequency and short wavelength involve the dynamics of individual molecules to a much greater extent than at the familiar low frequencies and long wavelengths.

Another direction in which the present theory will be extended is to include nonlinear irreversible processes. It is known already that nonlinear effects are important in some rheological situations, for example, the flow of polymer solutions; but so far there is very little worked out statistical mechanical theory of the appropriate hydrodynamic equations. A modest begin-

ning would be to estimate the magnitude of rate of shear needed to get appreciable nonlinear effects in, say, a gas at low density.

Nonlinear effects are of the greatest importance in chemical kinetics; the theory due to Yamamoto that was described earlier was limited to small deviations from equilibrium. One would like to be able to estimate how large a deviation from equilibrium must be to invalidate familiar methods. Also, in the kinetics of very fast reactions, it is probably important to take into account frequency dispersion of the rate constant. This has never been done.

Perhaps the most valuable use of time-correlation functions will be in relating different transport coefficients and thermodynamic properties. An example is the discussion of the Wiedemann-Franz law by Chester & Thellung. This kind of investigation is particularly valuable when it does not require explicit calculation of transport coefficients, but only knowledge of the structure of the transport coefficient formulas.

One example which will prove of great value is in the theory of ionic solutions. Electric conductivity is given by a well defined time-correlation function expression. Experiments and previous theoretical work suggest a strong relation between ionic conductivity and viscosity. The viscosity coefficient is also given by a time-correlation function expression. It is natural to hope that some direct connection will be found, independent of special models or detailed calculations.

The success of Eyring's theory of absolute reaction rates is well known. In some circles, however, this theory is in disrepute because it does not stand as the first step in a well defined sequence of approximations. I expect that in the next few years, the relation of Eyring's methods to time-correlation function methods will be clarified. Probably, the theory of viscosity in dense media will be developed by finding some kind of "reaction path" in phase space which will dominate the time dependence of the appropriate time-correlation function.

In conclusion, I expect that most of the progress in this field during the next few years will come from analysis of the structure of time-correlation function formulas, rather than from actual calculation.

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